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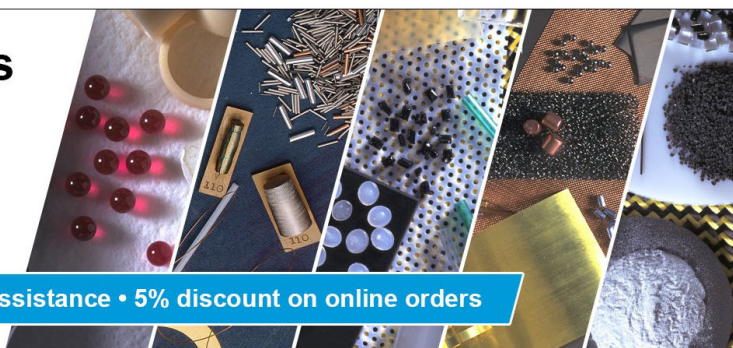
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Note: Production of silver nanoclusters using a Matrix-Assembly Cluster Source with a solid CO₂ matrix

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The production of nanocluster beam has been a subject of intense research since the first cluster beam sources were reported in the 1950s. Clusters of virtually any material have been produced with size control that goes down to a single atom.¹ The high control levels have compromised the number of clusters produced, which is one of the main obstacles to exploring cluster properties in applied areas. Recent developments, however, have allowed a cluster current of the order of a few nA and deposition rates of nm/s.^{1–5}

A new type of high flux cluster source is the Matrix-Assembly Cluster Source (MACS).^{6,7} MACS exploits cluster formation inside a solid rare gas matrix^{8–10} and has great potential for scaling up cluster production by orders of magnitude. The matrix is a copper square of side 2.5 cm cooled down to a cryogenic temperature of around 20 K, using a closed cycle cryocooler (SHI, CH-202 10 K). Atoms of the material of interest are evaporated from a thermal effusion cell (Createc, HTC-63-10-2000) and co-condensed with gas atoms/molecules forming a solid film that is later sputtered by an ion beam (Tectra, Gen2 plasma source).

The matrix serves as a cooling medium for cluster formation while the ion beam sputtering accomplishes two distinct goals, (i) it provides the required energy for the atoms to collide inside the matrix and agglomerate into clusters and (ii) it ejects the clusters formed, allowing them to be deposited on a substrate. Changing the metal loading in the matrix tunes the cluster size, which can range from hundreds to thousands of atoms for metal loadings of ~1% to 5% in the case of Ag in Ar.⁷ The produced clusters are deposited on to transmission electron microscopy (TEM) grids positioned approximately 5 cm away from the matrix. The matrix is angled at 45° to the ion beam and deposition stage, as illustrated in Figure 1.

One practical limitation to the further scaling up of the MACS approach to industrial levels is the temperature required to condense the gas matrix, <20 K for solid Ar. Here we report the replacement of the argon used to date with CO₂, which would allow condensation at 80 K so that liquid nitrogen can be used as a cooling agent instead of liquid helium.

The clusters produced were analysed via high-angular annular dark field (HAADF) images in an aberration-corrected scanning transmission electron microscopy (STEM); the JEM-2100F (Jeol) was operated at 200 kV. Figure 2 shows STEM images and the corresponding size distributions for a range

of metal loadings and ion beam energies. These samples correspond to silver clusters produced from a CO₂ matrix that was built for 5 min at a pressure of 8.0×10^{-6} Torr. Particle size distributions obtained in reference to the intensities of size-selected gold clusters show that one can correlate the number of atoms inside a cluster with the integrated HAADF intensity.¹¹ To determine the size distribution of the samples in the present work, we used the HAADF intensities of single Ag atoms as the reference. Single atom intensities were acquired from high-resolution images; due to beam damage, it is common to find some of them in the vicinity of a particle. A set of atoms is measured, a Gaussian is fitted to the intensity distribution, and the average used as the single atom intensity.

For Figures 2(a)–2(d) the temperature of the evaporator was changed to alter the deposition rate and thus the metal loading in the matrix. Four different deposition rates were analysed, 0.2 Å/s, 0.3 Å/s, 0.5 Å/s and 0.9 Å/s, corresponding to a matrix loading of 4%, 8%, 14%, and 23% (number of silver atoms compared with CO₂ molecules). The matrix was sputtered by an ion beam of 1 keV and with ~50 μA for 2 min intervals, during which the clusters formed were deposited on the TEM grids. The histograms present asymmetrical peaks characteristic of lognormal distributions, which were fitted to the graphs (solid line) in Figure 2. The mean sizes of the clusters in ascending order of metal loading are 79, 83, 86, and 175 atoms. The peaks of the distributions are at 25, 27, 25, and 28 atoms, values extracted from the fit.

The size distributions are not very sensitive to the metal loading in the matrix. For metal loadings of 4% to 14% the size distributions are largely similar, with a mean cluster size of approximately 80 silver atoms, for higher concentrations

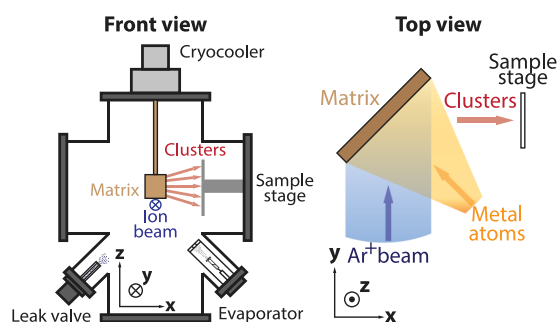


FIG. 1. Schematic illustration of the Matrix-Assembly Cluster Source showing the key components and geometry.

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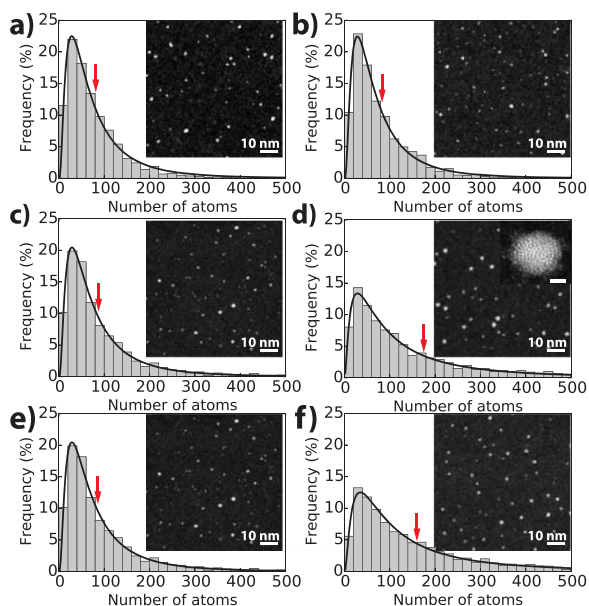


FIG. 2. Size distribution and HAADF-STEM images of the samples prepared from CO₂ matrices with different Ag loadings, (a) 4%, (b) 8%, (c) 14%, and (d) 23% and ion beam energies, (e) 1 keV and (f) 2 keV. A lognormal distribution fit (solid line) is shown with the average cluster size indicated by an arrow. High-resolution image of a single cluster is seen on the inset, scale bar corresponds to 1 nm.

in the matrix the mean size shifts to 175 Ag atoms. This behaviour is different from the previous work when an argon matrix was used.^{7,10,12} A possible reason for the difference in the size distributions relates to the diffusion of Ag atoms during matrix formation. The bonding energy of Ag in Ar is ≈ 0.2 eV,¹³ whereas for Ag in CO₂ is on the order of 1 eV.¹⁴ It seems that silver atoms may diffuse more easily in an Ar matrix than in CO₂, thus making the initial cluster size (before sputtering) more dependent of loading conditions.

Figures 2(e) and 2(f) show the cluster production for a matrix with 14% of Ag and two different ion beam energies, 1 keV and 2 keV. We see the formation of bigger clusters, leading to broadening of the lognormal distribution for the higher beam energy. Average cluster size nearly doubles from 86 to 160 Ag atoms and the peak position shifts from

25 to 33 atoms. An average cluster current of 0.15 ± 0.02 nA was obtained, which is smaller than the values reported for an Ar matrix.^{6,7}

In this short article, we demonstrated that Ag clusters with up to a few hundred atoms have been generated from a condensed CO₂ matrix. Although the experiments were conducted at a temperature of 20 K, the use of CO₂ means MACS operation should be viable at higher (liquid nitrogen) temperatures. Cluster size seems to depend less on metal loading in the matrix than previous response for an Ar matrix⁷—an effect which may be due to reduced diffusion prior to sputtering—but cluster size is sensitive to ion beam energy.

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